Technical note

The band gap pressure coefficient of CuInTe$_2$

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Abstract

The band gap pressure coefficient of CuInTe$_2$ at room temperature has been measured to be 53 meV/GPa in contrast to the value of 22 meV/GPa reported previously by Gonzalez and Rincon (J. Phys. Chem. Solids, 51 (1990) 1093). The new coefficient is in good agreement with the theoretical value predicted by Wei et al. (Phys. Rev. B, 58 (1998) R1710). © 2001 Elsevier Science Ltd. All rights reserved.

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In a recent paper Wei et al. [1] reported a first-principle calculation of the band gap pressure coefficients (dE_g/dP) in a series of semiconductors with the zincblende and chalcopyrite structure. They found good agreement between the experimental and calculated band gap pressure coefficients except for CuInTe$_2$. In that case the experimental value [2] was lower than the calculated value by more than a factor of two. This has led Wei et al. to cast doubt on the experimental value and to call for a new measurement of dE_g/dP in CuInTe$_2$. We have performed such a measurement and found that the absorption edge of CuInTe$_2$ has a linear pressure coefficient of 53 meV/GPa in good agreement with the prediction of Wei et al. [1].

Our experiment was performed on single crystals of CuInTe$_2$ grown by the horizontal Bridgman method. The purity of the elements is 5N for Cu, In and Te. From X-ray diffraction (XRD) measurements using the powder method, the chalcopyrite structure was confirmed. Samples were lapped to a thickness of ~40 μm and cut to rectangular pieces of about $200 \times 200 \ \mu^2$ in size for absorption measurements inside a gasketed diamond anvil cell (DAC). The pressure medium was a mixture of

methanol and ethanol while the pressure was measured by the standard ruby fluorescence technique. The pressure distribution inside the cell is determined typically by placing three ruby chips within the hole in the gasket. Pressure variation was found to be less than 0.1 GPa. The absorption measurements were all performed at room temperature. Care was taken to eliminate as much as possible any stray light bypassing the sample. The absorption spectra of the sample were found to be essentially the same both inside and outside the DAC. The latter measurement was performed with a much larger sample so that stray light was not a problem. With the sample inside the DAC the highest absorption coefficient we could measure was smaller than outside the cell as a result of stray light which could not be eliminated.

For ease of extrapolating the band gap from the measured absorption spectra, we have plotted in Fig. 1 the square of the absorption coefficient versus the photon energy for several pressures. Notice that the shape of the absorption edges remains unchanged under pressure indicating that there is no significant increase in pressure inhomogeneity. This also means that the pressure coefficient of the band gap can be determined by the *shift* of the whole absorption curve without regard to the methodology of extracting the absolute value of the band gap from the absorption spectra. We have estimated the band gap E_g simply by extrapolating the linear part of the curves in Fig. 1 to zero absorption.

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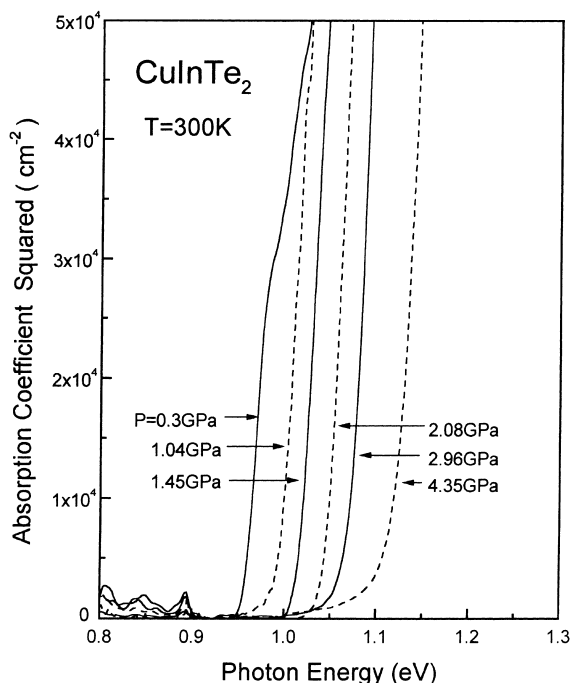
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Fig. 1. The absorption coefficients squared of the CuInTe$_2$ sample measured inside the DAC at several different pressures.
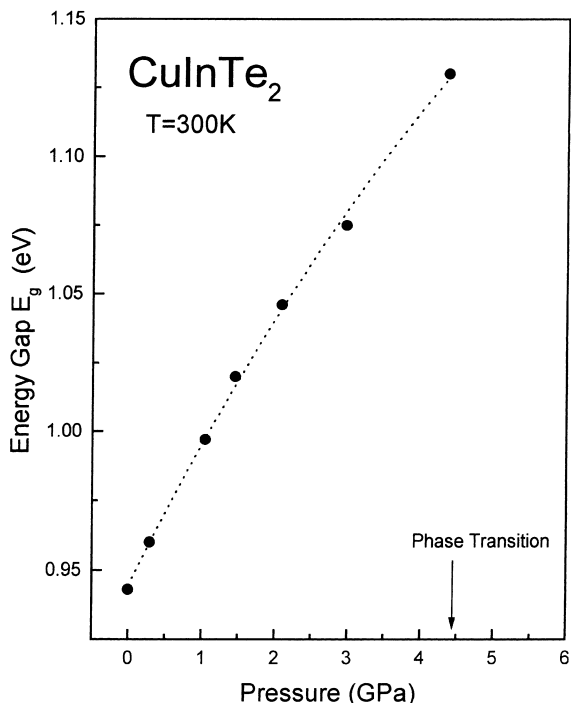

Fig. 2. Plot of the band gap of the CuInTe$_2$ sample versus pressure. The vertical arrow indicates the pressure when the sample undergoes a phase transition as observed optically.

The pressure dependence of the CuInTe$_2$ band gap deduced in this way is shown in Fig. 2. We found this dependence to be slightly nonlinear. To determine the linear part of the band gap pressure coefficient ($\alpha = dE_g/dP$), we have fitted E_g with a quadratic equation:

$$E_g = E_0 + \alpha P + \beta P^2 \qquad (1)$$

and obtained $E_0 = 0.945$ eV, $\alpha = 53$ meV/GPa, and $\beta = -2.6$ meV/(GPa)^2. The plot of Eq. (1) with these parameters is shown as the broken curve in Fig. 2. The nonlinearity may be caused by a semiconductor to metal phase transformation reported previously by Gonzalez and Rincon [2] and by Range et al. [3]. We have also observed a sudden transformation of the sample to an opaque phase at $P = 4.6$ GPa. This transition pressure is much higher than the value of 2.8 GPa reported by Gonzalez and Rincon [2] and the value of 2.0 GPa obtained by X-ray measurements at 570°C [3]. On the other hand, recent high-pressure XRD studies in CuInTe$_2$ [4] suggest a transformation from the chalcopyrite to a cubic NaCl-type structure at 5.9 GPa. The reason for these differences in the phase transition pressure is not completely clear at this point.

There can be a number of possible reasons to account for the difference in the pressure coefficients of CuInTe$_2$ measured by us and by Gonzalez and Rincon [2]. One possibility is the different pressure calibration. However, this explanation cannot account for both the lower pressure coefficient obtained by Gonzalez and Rincon [2] and their lower phase transition pressure. Another possibility is the different sample quality, such as the presence of below-band-gap absorption due to defects and/or impurities. The pressure coefficients of deep centers in chalcopyrites are often different from those of the band gap; see for example Ref. [5]. Indeed Wasim et al. [6] have recently studied the Urbach tails in CuInTe$_2$ samples with different amounts of defects as a result of deviations from stoichiometry. In general, the Urbach tail is more important in the region below the band gap where the absorption coefficients are smaller. In the CuInTe$_2$ sample studied by Gonzalez and Rincon [2] the absorption coefficient was measured with a Jobin Yvon spectrometer. In the same paper they also reported a measurement of the band gap pressure coefficient in CuGaS$_2$ and CuGaSe$_2$ using a Coderg Triple Monochromator. Presumably this monochromator had lower stray light level than the one used for the CuInTe$_2$ sample so they were able to measure much larger absorption coefficients in both CuGaS$_2$ and CuGaSe$_2$. The pressure coefficients of the band gap for these two chalcopyrites were in good agreement with other reports [5].

The significance of the agreement between the theoretical and experimental band gap pressure coefficients (α) in CuInTe$_2$ is that it helps to establish a trend in α among the chalcopyrites. As pointed out by Wei et al. [1], α increases strongly in the series: I–III–S$_2$ $\Rightarrow$ I–III–Se$_2$ $\Rightarrow$ I–III–Te$_2$. This trend has so far

been observed in the $CuGaVI_2$ series and the $AgGaVI_2$ series [2,7]. The result of Gonzalez and Rincon [2] in $CuInTe_2$ violates this trend and hence casts doubt on the theoretical result. Our result, on the other hand, suggests that the $CuInVI_2$ series obeys this trend rather well.

In conclusion, we have measured the pressure dependence of the absorption edge in single crystals of $CuInTe_2$ by using a DAC. We have found that the linear pressure coefficient of the band gap in this semiconductor to be in good agreement with the theoretical prediction of Wei et al. [1].

Acknowledgements

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